SOL- GEL SYNTHESIS OF BOROSILICATE VITRIFIED BOND FOR DIAMOND GRINDING WHEEL

A project submitted

By

SUSRI SANGEETA

(108CR044)

In the partial fulfilment of the requirements of degree

Of

Bachelor of Technology

DEPARTMENT OF CERAMIC ENGINEERING

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CERTIFICATE

This is to certify that the thesis entitled, "Sol-gel synthesis of borosilicate vitrified bond for Diamond grinding wheel", submitted by **Ms Susri Sangeeta (Roll no. 108CR044)** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

Date:

Dr. Japes Bera
(Head of the Department)
Dept. of Ceramic Engineering
National Institute of Technology
Rourkela-769008

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Susri Sangeeta

108Cr044

ABSTRACT

Vitrified bond diamond composites were prepared by using commercial diamond grits and a low melting sodium borosilicate glass vitrified bond. Sodium borosilicate glass with composition: 50 SiO_2. 20 B_2O_3 .10 Al_2O_3. 10 Na_2O, 8 K_2O and 2 ZnO (mol%) was synthesised through sol-gel process using TEOS , Boric acid , $NaNO_3$, Al_2O_3, KNO_3, $Zn(NO_3)$ and HNO_3 as catalyst.

Thermal decomposition behaviour of gel was studied using TG & DSC. The glass forming temperature was identified and characterised by XRD studies at different stages. Initial gel shows very little boron in glassy network. A complete amorphous glass was obtained heating the gel at 700˚C.

Calcined glass powder was used as a bonding material for diamond grits. Bonding behaviour between diamond & glass was investigated by optical microscopy. An optimal amount of vitrified bond for diamond grits with 250 micron was 5:2 (wt%) diamond: bond and sintering the composite in air atmosphere at 650 to 700 ^oC.

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CHAPTER 1

INTRODUCTION

Diamond abrasive tools are superhard composite materials having high abrasive performance. They have high hardness, excellent abrasion resistance and good thermal conductivity. For these advantages, diamond abrasive tools have high demands for high speed, high efficiency and high precision machining and grinding industry nowadays.

This composite is composed of diamond grits and bonding matrix. There are three types of bonding materials normally used for the composite; metal, resin and vitrified glass bonds [1][2][3]. The strength of resin bond is lower than metal or vitrified bond. That is why they exhibit higher wear. Resin bonded diamond tools are fabricated by hot pressing which produce a matrix without pores as well as resin bonds cannot be used for the abrasive grit size lower than 2 microns, as the grains are pushed inside the resin bond during grinding.

Metal bonded wheels have higher bonding strength than resin bonded wheels. Metal bond matrix is generally composed of bronze. Again diamond-bronze composite is fabricated by hot pressing. For this reason, they have low porosity in the matrix which reduces the grinding efficiency due to the rise in work-piece temperature by severe friction between metal bond and work-piece. That is why they can grind fewer parts per hour than vitrified glass bonded tool. Further, metal bonded tool can contaminate surface of work-piece thereby limiting their use in electronic devices.

As stated above, vitrified bonded tools have higher stiffness and low degradation resulting a better tolerance and flatness in the product. Also increase number of parts can be prepared per wheel. However, they do not have sufficient self-dressing ability due to low porosity. Present investigation aims to synthesize the vitrified bond by sol-gel process as gel inherently has high porosity, the bond matrix will have enough porosity to increase the efficiency of the tool.

CHAPTER 2

LITERATURE REVIEW

There are many patents documents available for vitrified bond tools of different varieties and method of their manufacturing. Some patents are U.S. 7,044,990 B2 [4], US 2009/0011198 A1 [5] and US 2009/0313906 A1 [6].

Diamond is the hardest material widely used in cutting tool, abrasive tool etc. Diamond particles are embedded in a bond material for its application as tool. As stated above, the vitrified bond has higher ability and strength to hold abrasive grains. Vitrified bonds are usually high melting material and diamond grits are oxidized easily during the sintering of vitrified bond. To avoid this, low melting bonds must be used which have the sintering temperatures in the range 700-900 ˚C. A sintering temperature less than 700 ˚C will be preferred to protect the oxidation of diamond. Usually borosilicate glass is used as vitrified bond due to its low vitrification temperature and high strength.

Borosilicate glass based bond powders are conventionally prepared by quenching the molten glass [7] [8] [9]. As discussed, the porosity plays an important role in grinding. For that high porosity vitrified super abrasive products and its method of preparation has been patented (US patent 61/132, 808, field Jun 23, 2008). Porosity controls the contact area between the work-piece and the composite microstructure. Porosity also felicitates movement of coolant around the microstructure which keep the grinding surface temperature as low as possible.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 SYNTHESIS OF BOROSILICATE GLASS:

Borosilicate glass (composition shown in Table 1) was synthesized through sol gel process using Tetra-ethyl ortho silicate (TEOS) (MERCK) as silica source, boric acid (HDFCL) for B_2O_3, Aluminium nitrate (HDFCL) for alumina source, Sodium nitrate (HDFCL) for Sodium oxide source, Potassium nitrate (RANKEM) for Potassium oxide source and Zinc nitrate (HDFCL) for Zinc oxide source. Ethanol and distilled water were used as solvent.

Table 1. Composition of Borosilicate Glass used in the study (mol %)

SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	ZnO
50	20	10	10	8	2

What everything does??

- Tetra Ethyl Ortho Silicate is the source of silica
- Water hydrolyses the TEOS so that it can polymerize.
- Ethanol is a co-solvent that is miscible with both TEOS and water to get both into the same phase so they can react.
- Nitric acid is a catalyst that helps hydrolysis more quickly.

The sol- gel glass preparation is shown in flow-chart Fig. 1.

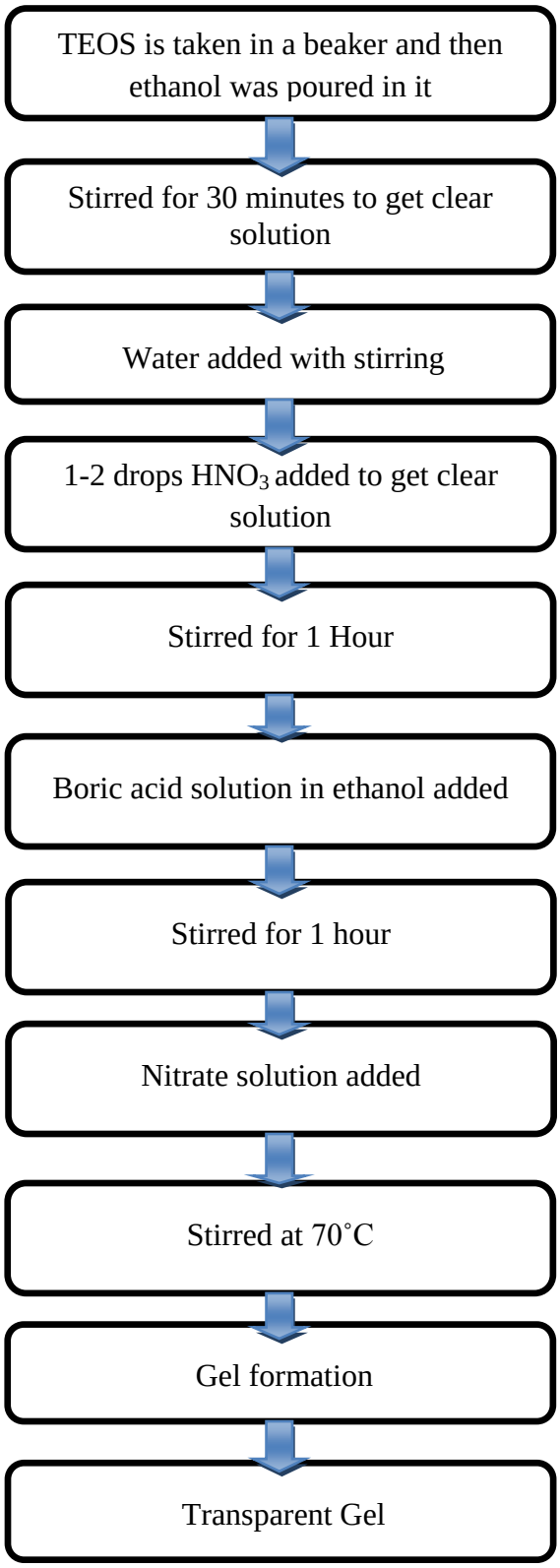

Fig. 1 The procedure for the preparation of sol- gel glass

In details the procedure is as follows:

1. A solution of Tetra Ethyl Ortho Silicate (TEOS), ethanol and water was taken in a beaker such that the ratio of Water to TEOS was 16:1 and that of water to ethanol was 10:90.This solution was stirred regularly until a clean solution was obtained. Then 1.8185 g of boric acid was dissolved in ethanol in a different beaker. After the complete dissolution of boric acid in ethanol, this solution was mixed with the initial solution of TEOS, Ethanol and Water. Furthermore, 0.1 M nitric acid (HNO_3) was added to the solution drop wise until the solution becomes clear. Then in separate beakers 0.0675 g of aluminium nitrate, 1.371 g of sodium nitrate, 0.858 g of potassium nitrate and 0.229 g of zinc nitrate were dissolved in water. After complete dissolution in water, all the nitrate solution were mixed and poured in the initial solution. After this the solution was stirred at 70 ˚C. Gelling should start after sometime and the above prepared sol should convert to transparent gel.

   RESULT: Gel was not obtained due to higher concentration of ethanol i.e. 1:90 TEOS: Ethanol. Then the process was modified by using that ratio 1:11 as follows:

2. First 9.22 ml of Tetra ethyl ortho silicate (TEOS) was taken in a beaker. Then 225.23 ml of ethanol was added to it. That is, the ratio of TEOS to ethanol was 1:11. The above solution was stirred with the help of a magnetic stirrer for 30 minutes to get the clear solution. Then 1.5 ml of water was added to the prepared solution. Furthermore, 6-7 drops of 0.1 M nitric acid (HNO_3) was added to get pH-2 and the solution was stirred till it becomes clear. Simultaneously, in a separate beaker, 1.8185 g of boric acid was dissolved in ethanol. After the complete dissolution of boric acid in ethanol, this solution was poured in the initial solution containing TEOS, ethanol and water. Again the solution was stirred for 1 hour to get

the clear solution. Then nitrate solution was prepared by dissolving 0.0675 g of aluminium nitrate, 1.375 g of sodium nitrate, 0.858 g of potassium nitrate and 0.229 g of zinc nitrate in water separately in a beaker. After which all the nitrate solution were mixed and poured in the initial beaker. The above prepared solution was then stirred at 70 ˚C. After sometime the water should evaporate and the process of gelling should start. Here didn't have a complete transparent gel rather a translucent gel was obtained after stirring at 70 ˚C. The gel formed through this procedure has been shown in Fig. 2.

RESULT: The Gel prepared was translucent again due to higher concentration of ethanol. Accordingly, the process was changed by using that ratio 1:2 as follows:

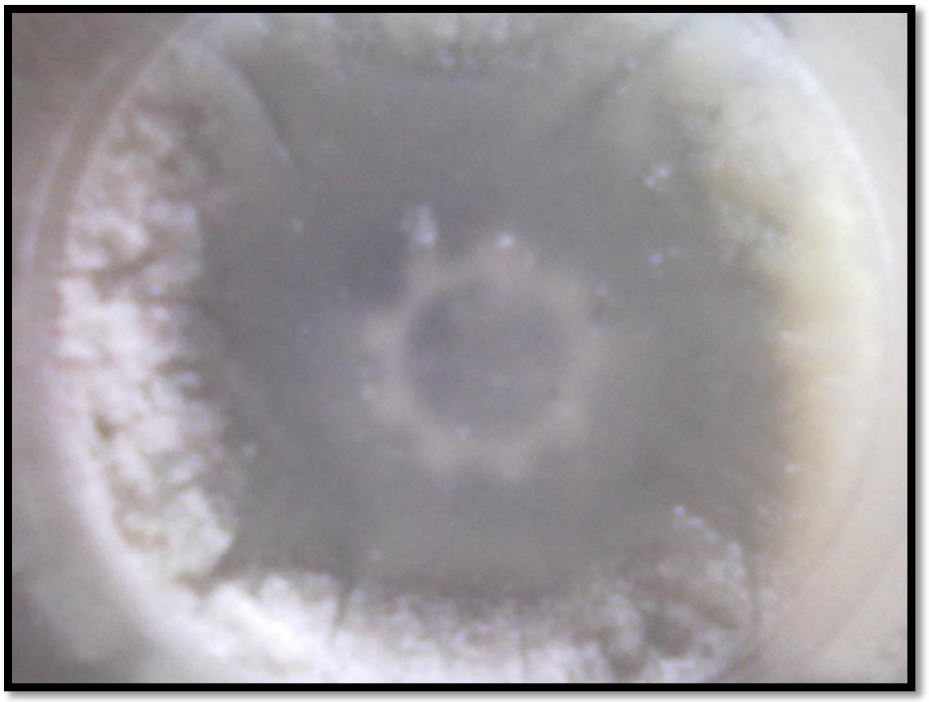

Fig. 2. The translucent gel formed through the sol-gel process

3. First, 37.213 ml of Tetra ethyl ortho silicate was taken in a beaker. Then 19.43 ml of ethanol was added to it. Here for 1 mol of TEOS we took 2 mol of Ethanol. The above solution was stirred with the help of a magnetic stirrer for 30 minutes to get the clear solution. Then 6 ml of water was added to the above prepared solution. After which 6-7 drops of 0.1 M nitric acid (HNO_3) was added to get pH-2 and the solution were stirred till it becomes clear. Simultaneously, in a separate beaker, 7.274 g of boric acid was dissolved in ethanol such that boric acid is dissolved completely in ethanol. After the complete dissolution, this solution was added to the initial solution once the solution becomes clear. Again the solution was stirred for 1 hour to get the clear solution. Then nitrate solution was prepared by dissolving 0.27 g of aluminium nitrate, 5.484 g of sodium nitrate, 3.432 g of potassium nitrate and 0.916 g of zinc nitrate in water separately in a beaker. After that all the nitrate solution were mixed and poured in the initial beaker. The above prepared solution was stirred at 70 ˚C. After sometime it was observed that the volume of the solution became half and the process of gelling starts. Here we got a complete transparent gel after continuous stirring at 70 ˚C as shown in Fig. 3.

   RESULT: Complete transparent gel was obtained.

Fig. 3.The transparent gel formed through the sol-gel process

Reactions:

First hydrolysis of Tetra ethyl ortho silicate (TEOS) occur when TEOS and water is mixed in ethanol to get the silanol groups.

$$SiO(C_2H_5)_4 \longrightarrow Si\ (O\ C2H_5)_3\ (OH) + C_2H_5\ OH$$

Some catalysts preferably acids like nitric acid is used.

After hydrolysis, creation of Si-O-Si bond occurs that is condensation reaction takes place.

$$SiO(C_2H_5)_4 + Si\ (OC_2H_5)_3\ (OH) \longrightarrow (C_2H_5O)_3Si\text{-}O\text{-}\ Si(C_2H_5O)_3 + H_2O$$

Now polymerization reaction occurs that is the development of Si-O-Si bond in every direction accompanied by the production of H-O-H and R-O-H species.

CALCINATION AND SINTERING:

The prepared gel was then dried at 50-60 ˚C for 24 hours in a drier. After drying, the dried gel was manually crushed in an agate mortar till we get the fine powder. Then the fine powders was divided into 4 equal parts and were kept in separate alumina crucibles for calcining them at 500 ˚C, 600 ˚C, 700 ˚C with a soaking time of 2 hours each and one part is kept uncalcined for XRD analysis. Synthesis of one more batch of 60 g was done following the same procedure as that of third batch. This batch was calcined at 500 ˚C with a soaking time of 2 hours in a furnace. From the calcined batch, some amount of batch was mixed with 5% PVA solution which acts as binder for the green pellets. Then 3 samples each weighing 0.8 g was taken for pressing. For pressing, the die-punch was cleaned with acetone first and then stearic acid was used as lubricant. Pressing was done with the help of carver press at 3.5 ton with a dwelling time of 90 seconds each. The pressed pellet was then sintered at different temperatures as shown in Fig.4.

Pellet (a): at 700 ˚C with a soaking time 2 hours

Pellet (b): at 650 ˚C with a soaking time of 1 hour.

Figure 4: Pellets sintered at (a) 700 ˚C and (b) 650 ˚C

PREPARATION OF DIAMOND COMPOSITES:

The procedure for the preparation of diamond and the bond (borosilicate glass) composite is shown in flowchart (Fig. 5)

Trail 1:

1g of bond that is borosilicate glass prepared was mixed thoroughly for atleast 15 minutes with 5 g of diamond particles in an agate mortar. The size of the diamond particles used here are 250-300 microns (50/60 mesh size) as shown in Fig. 6. Then alcohol was added to the mixture in the agate mortar and mixed properly. After that, 6-7 drops of 5% PVA solution was added to the above prepared mixture and mixed with the help of a agate mortar. Simultaneously, the 20 volume percentage of the paraffin wax was dissolved in heptane and was poured in the mixture and mixed properly. Then the mixture was dried under the IR lamp for 5 minutes. The sample of

1g each was weighed and pressing of the sample was done in the carver press at 3.5 tonnes with a dwelling time of 90 seconds. After the pellets were prepared, these were sintered at 650 ˚C f with a soaking time of 2 hours and an intermediate holding at 400 ˚C (for binder burnout).

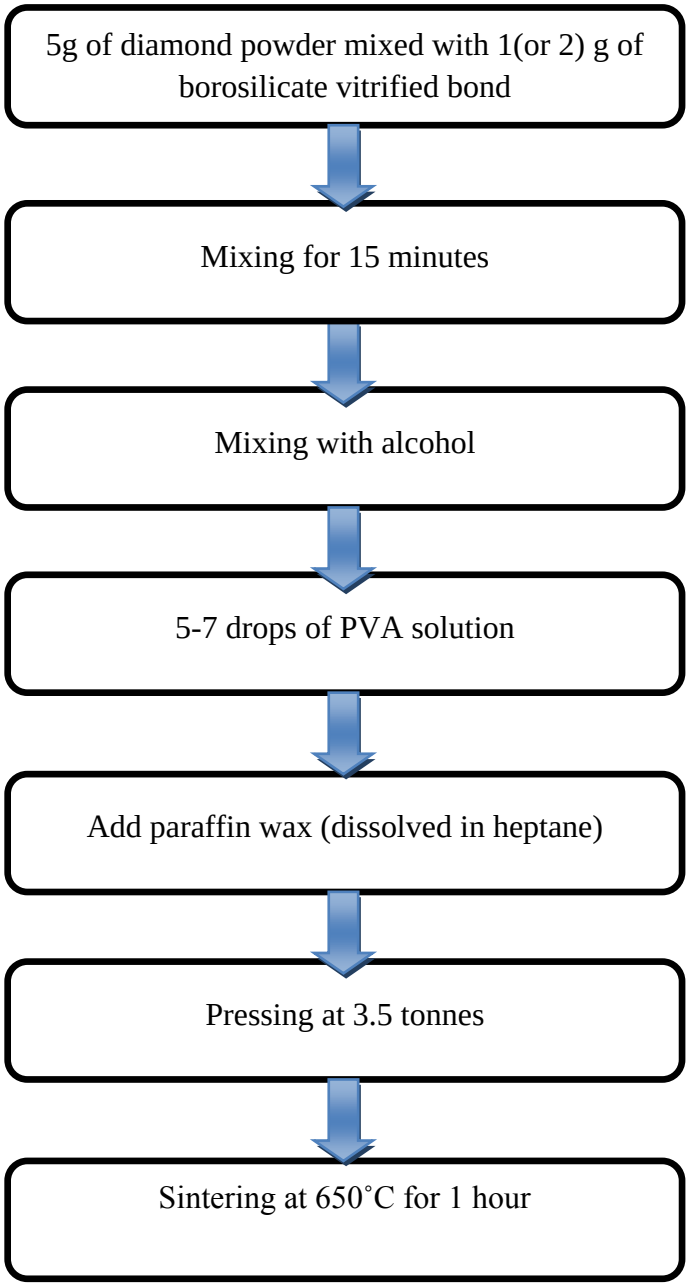

Fig. 5. Procedure for the preparation of diamond bond composite.

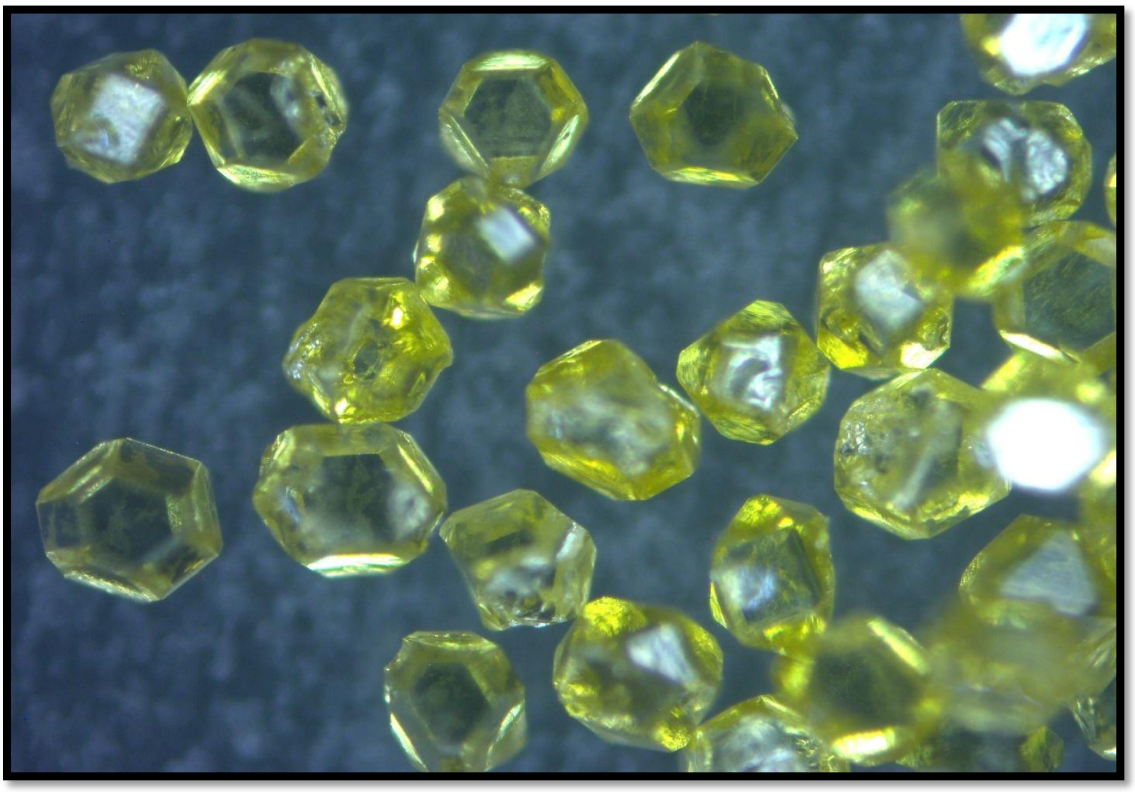

Fig. 6. The diamond grits used in the study

Trial 2:

Here, 2 g of bond was mixed thoroughly with 5 g of diamond powder for atleast 15 minutes in an agate mortar. Then alcohol was added to the mixture in the agate mortar and mixed properly. After that, 6-7 drops of 5% PVA solution was added to the above prepared mixture and mixed. Simultaneously, the 20 volume percentage of the paraffin wax dissolved in heptane was mixed. The mixture was then dried under the IR lamp for 5 minutes. The sample of 1 g each was weighed and pressing of the sample was done in the carver press at 3.5 tonnes with a dwelling

time of 90 seconds. The pellet was sintered at 650 ˚C with a soaking time of 2 hours and an intermediate holding at 400 ˚C (for binder burnout). The sintered pellet is shown in Fig. 7.

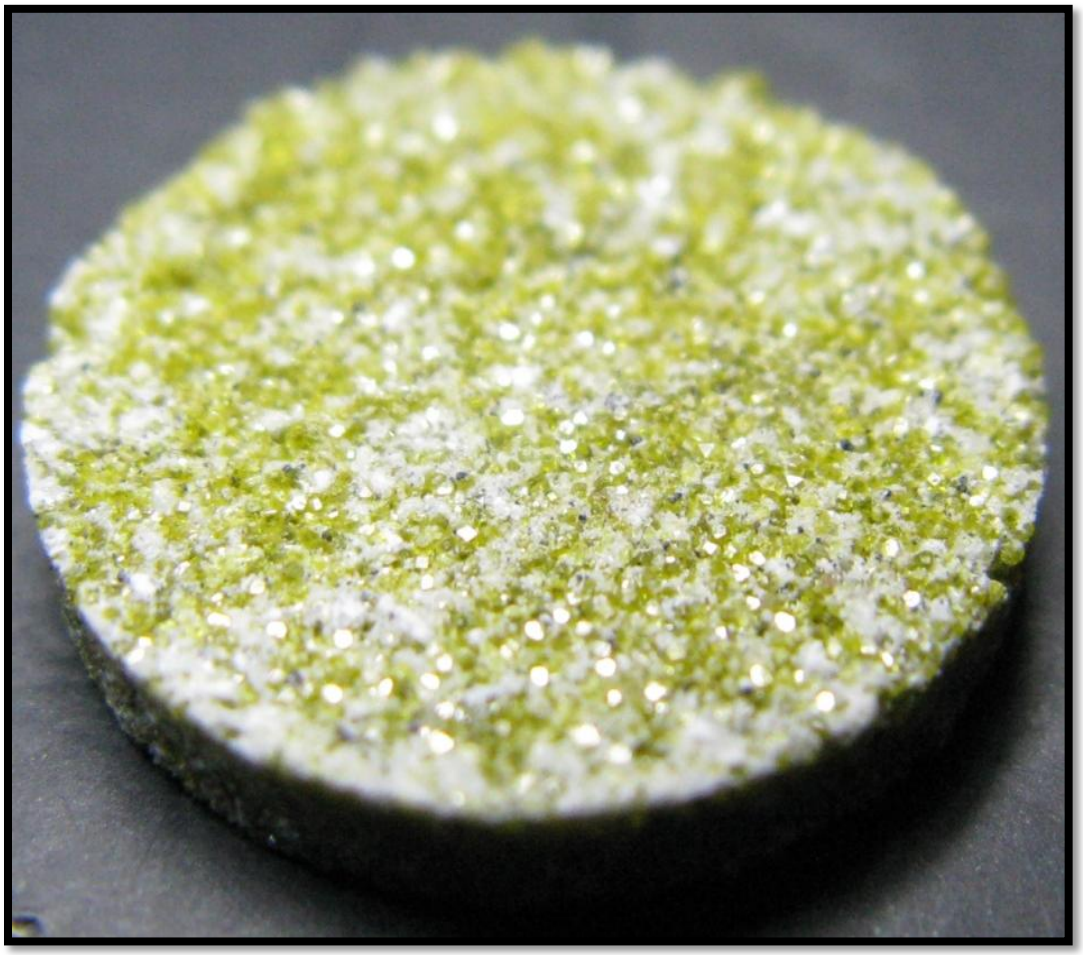

Fig. 7. Vitrified bond diamond pellet after sintering at 650 ^{o}C.

CHAPTER 4

RESULTS & DISCUSSION

Thermal Decomposition Behaviour:

Thermal decomposition of gel was studied using DSC (Differential Scanning Calorimetry) and TG (Thermo Gravinometry). TG shows the 18 % weight loss upto the temperature 150 ˚C with the DSC peak at 110 ˚C. This is due to the loss of water from the gel glass system. The second weight loss occur around 600 ˚C due to the decomposition of sodium nitrate, potassium nitrate from the system. During the decomposition of sodium nitrate and potassium nitrate, nitrogen gas evolves out from the system. Also the exothermic hump is due to the formation of network structure.

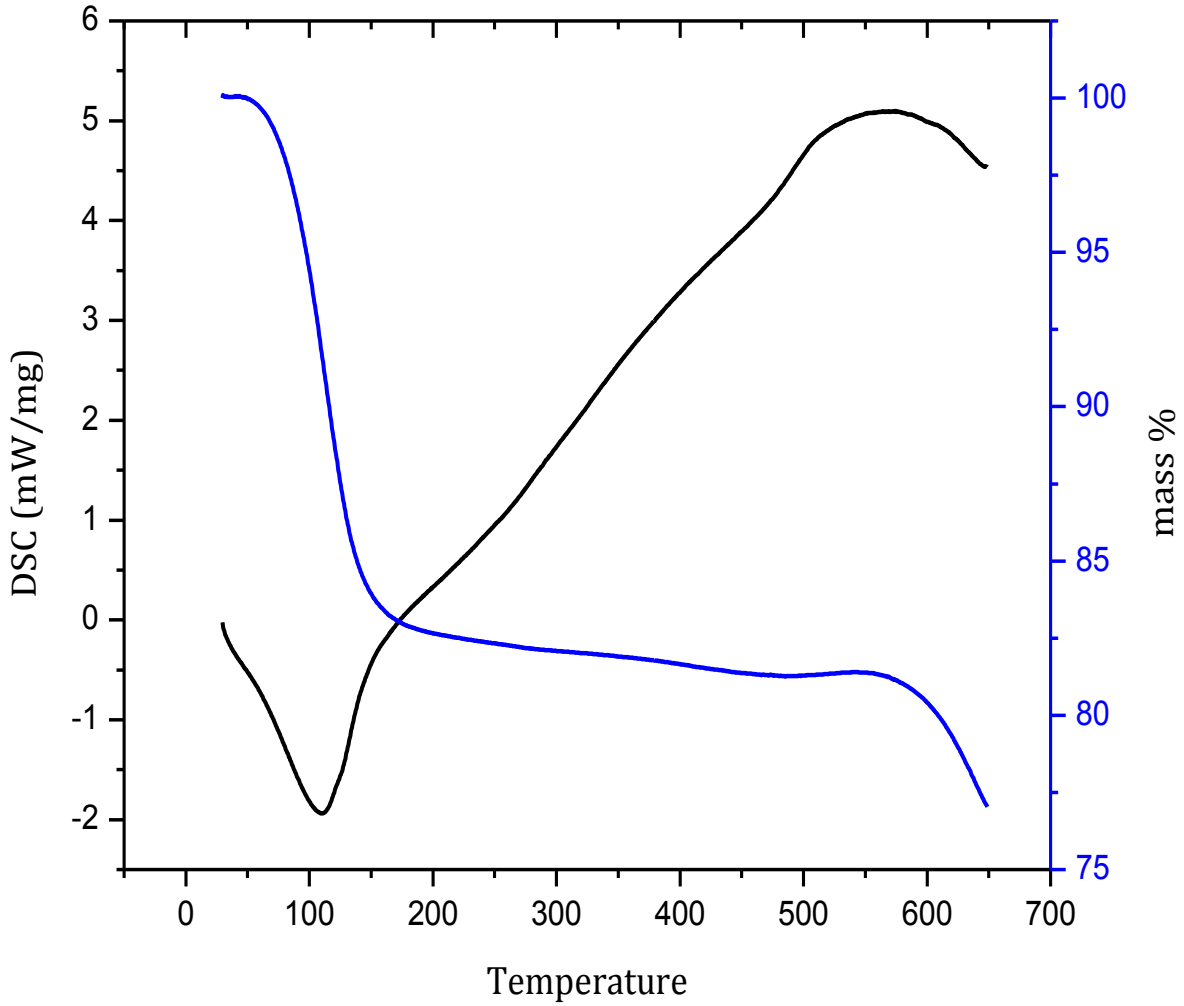

Fig. 8. DSC and TG plot for the sol-gel borosilicate glass powder.

Phase Formation Behaviour:

Fig. 9 shows the XRD pattern of as prepared gel powder and the powder calcined at 500, 600 and 700 ˚C. The raw powder shows crystalline peaks for boric acid.

Upon heat treatment, boric acid reacted with silica glass system. However, sodium nitrate and potassium nitrate based crystalline phases separated from the composition as an intermediate phase. These intermediate crystalline phases converted to amorphous glassy phases after final heat treatment at 700 ˚C. This indicates that the sol-gel process can be used for the preparation of borosilicate glass with different modifiers like Al_2O_3, ZnO, etc. The 2 mol % ZnO was used in the borosilicate glass composition to increase the wettability of basic glassy bond as reported by P.F. Wang et al.[7]. High wettability is favoured for the formation of glassy bond between diamond grains and to wet the diamond surface during the sintering process.

B_2O_3 are generally added into the glass composition to decrease the melting point of the glass.

Also the XRD analysis (shown in Fig. 10) of the pellets sintered at 650 ˚C and at 700 ˚C show similar phases. But the pellet sintered at 700 ˚C causes bloating (shown in Fig. 4) of the pellet. This bloating occurs due to the expansion of the material at high temperature. The reason is the presence of nitrate (decomposes around 700 ˚C) which produces nitrogen gas during their decomposition. But before their decomposition there is some vitrification of the body by which the surface pores are sealed and that is how the body expands. As a result the gases are responsible for this expansion.

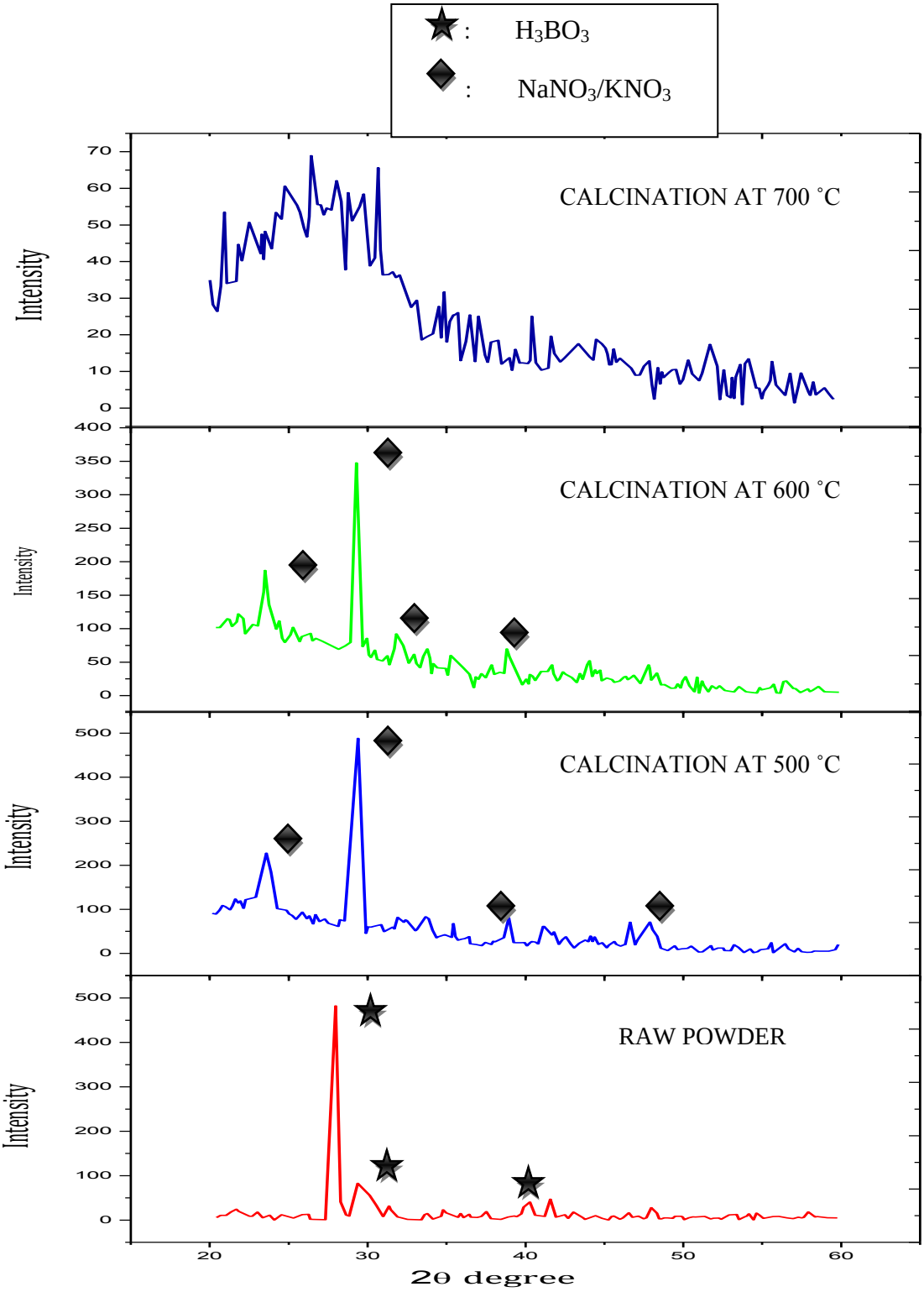

Fig. 9. XRD pattern of the raw gel powder and calcined at 500, 600, 700 ˚C.

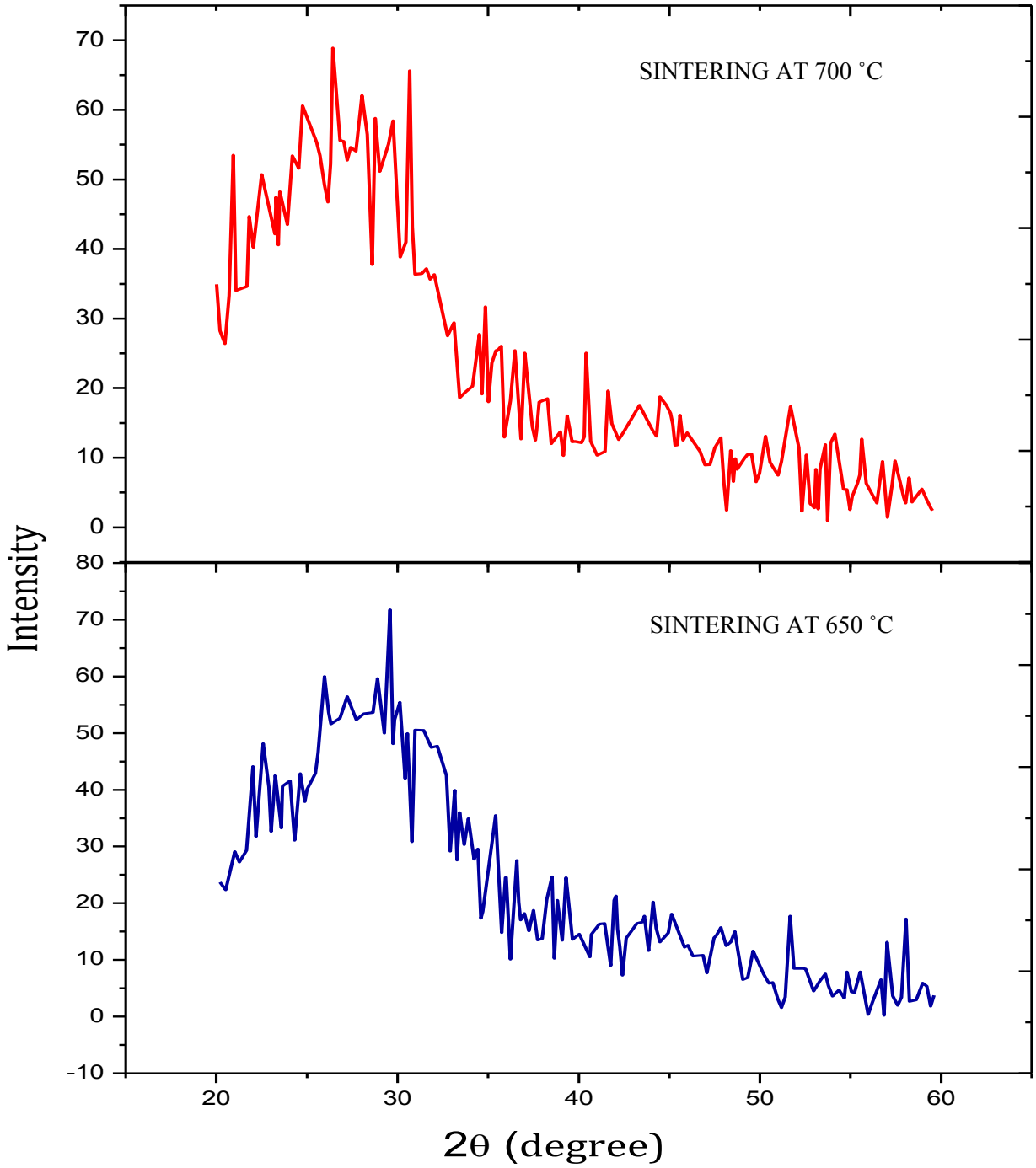

Fig. 10. XRD pattern of pellets sintered at 650 ˚C and 700 ˚C.

Optical Micrographs:

Fig. 11 shows optical micrograph of synthetic diamond grits and vitrified bonded diamond specimen with varying bond concentration.

The diamond grits used in the study were industrial synthetic diamond (ILJIN Diamond Co, ltd Korea) with 50/60 mesh (250-300 microns) grit size.

Fig. 11(a) shows the morphology of diamond grits which shows a relatively regular and smooth surface of typical diamond grits.

Fig. 11(b) and (c) shows the images of specimen sintered at 650 ^{o}C for 1 hour with an intermediate binder burnout at 400^{o}C for 2 hours. Both the images shows that the presence of vitrified bond (white phase) in between diamond grains. However, Fig. 3(b) shows inadequate bonding material between diamond grits as the composition was 5:1 wt % of diamond: bond. The figure also shows that the glass particles and diamond grits almost remain in their original particle size. While 5:2 wt % (diamond: bond) seems to be adequate (Fig. 3(c)). The bond between the diamond grits and the glass matrix was not strong as the glass did not have a large area of coverage on the diamond grits. This indicates that a longer sintering time and /or higher sintering temperature is necessary for the borosilicate glass system for 300 micron diamond grit size.

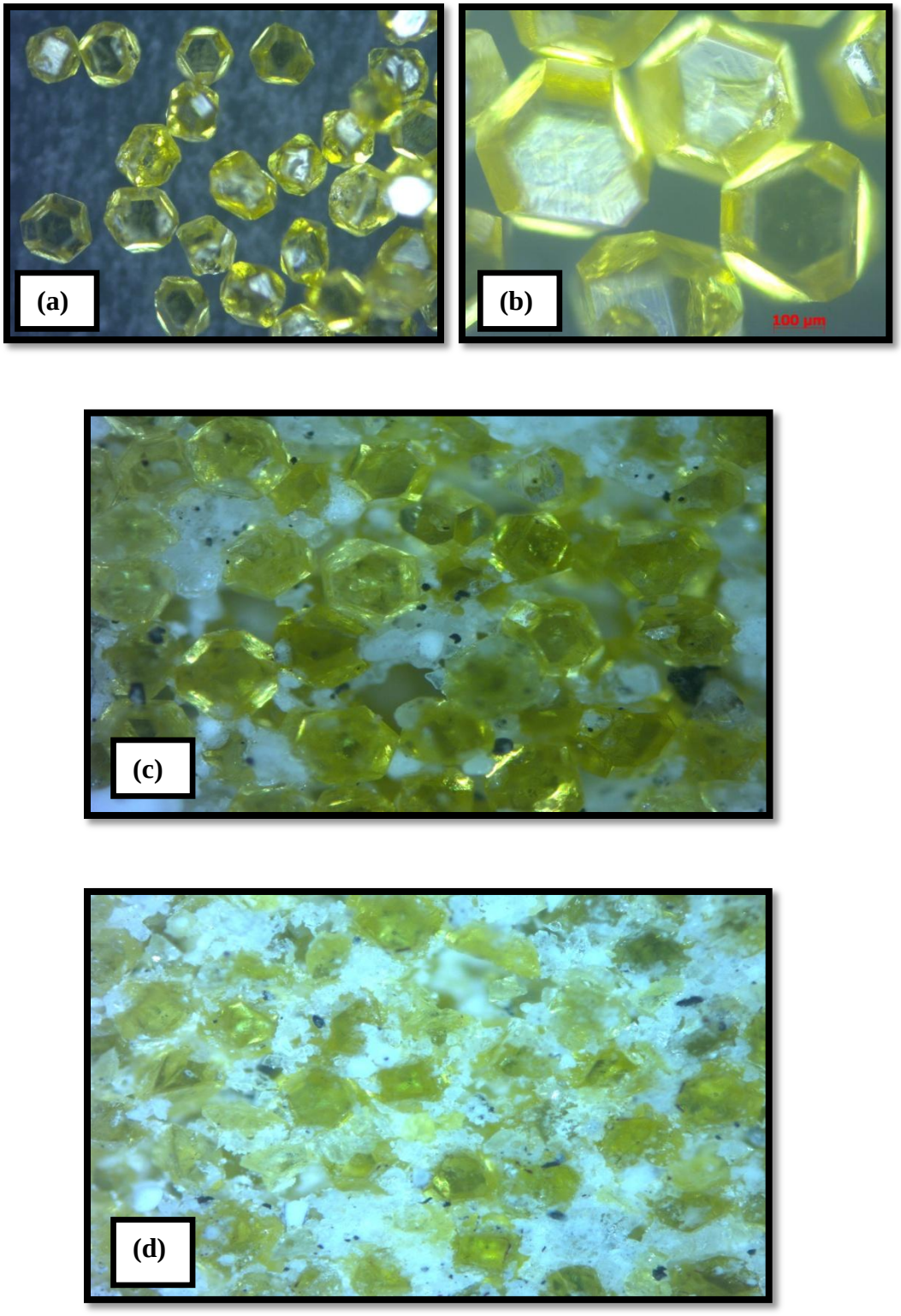

Fig. 11. Optical micrograph of (a) & (b) synthetic diamond grits (c) specimen with diamond: bond as 5:1 and (d) 5:2 wt %

CHAPTER 5

CONCLUSION

Sodium borosilicate glass with 10 mol% Al_2O_3 was successfully synthesised through sol-gel process using TEOS & Boric acid as major raw material. A complete transparent gel was obtained. The XRD pattern of gel shows the presence of boric acid as a separate phase indicating a nominal network formation of boron in the gel glass. The gel decomposes via reaction of Boric acid with silica glass, then intermediate separation of sodium, potassium nitrate and final amorphous glass formation at 650 ˚C. There were no crystalline peaks of either SiO_2 or other constituent in the final glass. Glass powder and diamond grits with 250 micron size were used to compact a green composite using paraffin wax as binder. The composition was successfully sintered at 650˚C with a diamond: bond ratio of 5:2.

CHAPTER 6

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